May 28, 1974 G. VILLARD 3,813,244

'ONIUM INDO-N-ARYLSULFOANILINE

Filed July 24, 1972 2 Sheets-Sheet 1

FIG. 3

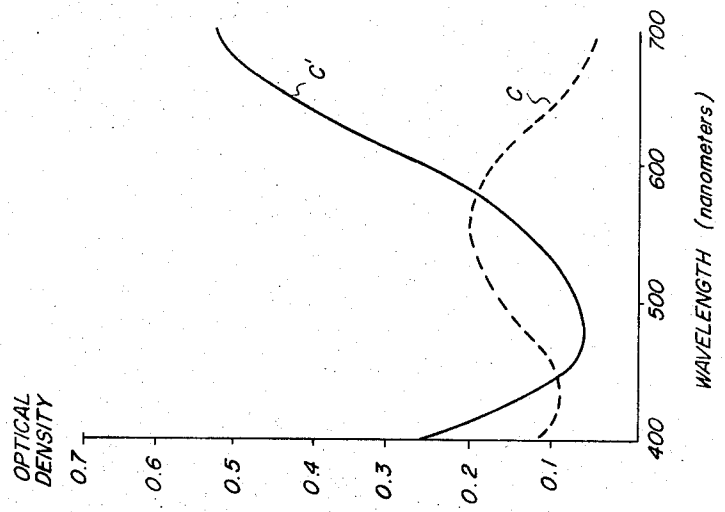


FIG. 2

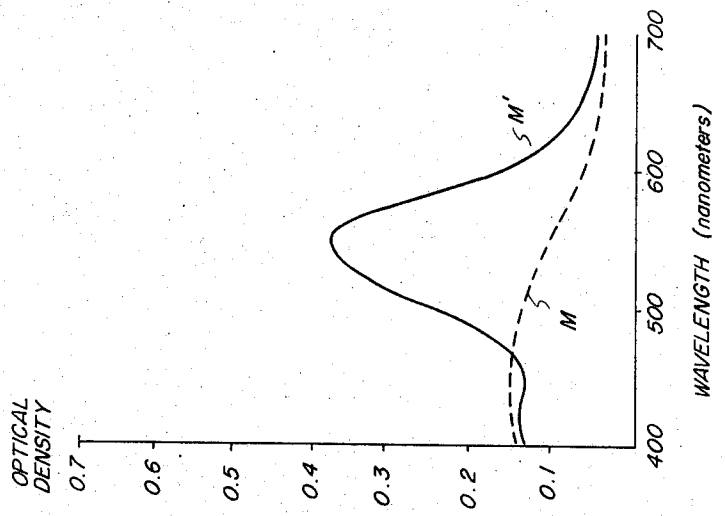
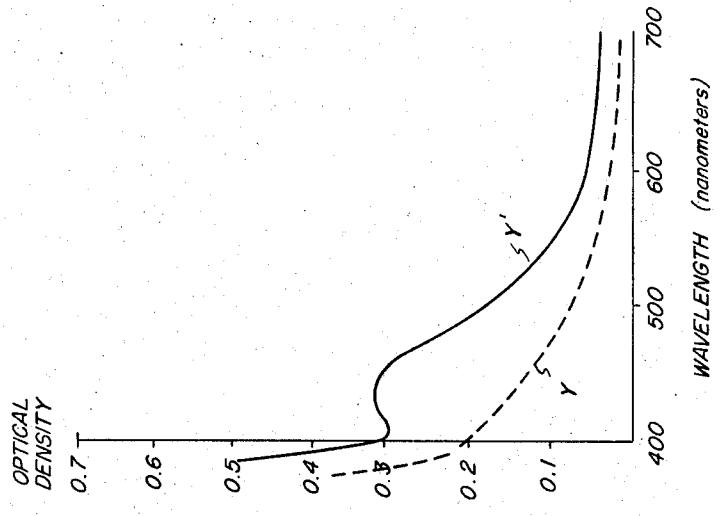


FIG. 1



'ONIUM INDO-N-ARYLSULFOANILINE

Filed July 24, 1972 2 Sheets-Sheet 2

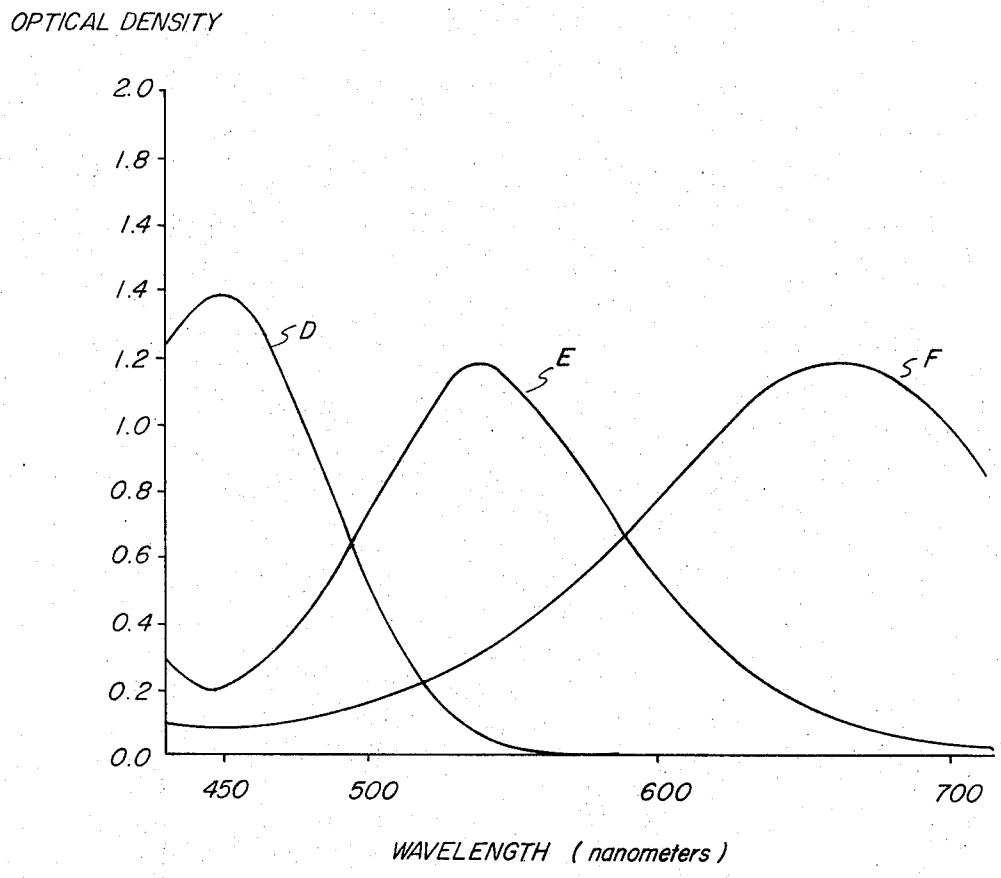


FIG. 4

United States Patent Office 3,813,244 Patented May 28, 1974

3,813,244

'ONIUM INDO-N-ARYLSULFOANILINE

George Villard, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y.

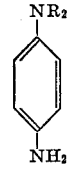
Filed July 24, 1972, Ser. No. 274,719
Int. Cl. G03c 7/00, 7/16, 5/54, 5/24, 1/76, 1/40
U.S. Cl. 96—3 20 Claims

ABSTRACT OF THE DISCLOSURE

'Onium indo-N-arylsulfoaniline compounds and processes of preparing them are disclosed. In one embodiment, improved photographic processes are described for forming indo-N-arylsulfoaniline dye images in photographic elements. Another embodiment relates to improved photographic elements containing 'onium indo-N-arylsulfoaniline image dyes. In yet other embodiment, image transfer systems and processes are disclosed wherein an 'onium-N-arylsulfoaniline image dye is formed during processing after imagewise exposure or wherein an o- or p-sulfonamidoaniline group is used to form the dye moiety, or dye precursor moiety of an image dye providing compound used in an image transfer system.

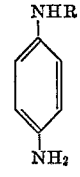
This invention relates to dyes, processes of making dyes, elements containing these dyes and precursors of these dyes, and processes for using elements containing said dyes and dye precursors.

Several procedures have been suggested in the prior art with respect to reaction of oxidized primary amino color developing agents with certain couplers to form dye images which are useful in photography, such as in substractive color processes. Several early patents discussed the possibility of using *p*-phenylenediamines and aminophenols as color developing agents. However, it soon became evident that p-phenylenediamines having one dialkyl-substituted nitrogen atom were regarded as the most practical color developing agent, as evidenced in "30 Years of Modern Colour Photography," *The British Journal of Photography*, July 15, 1966, 607; German Patent 253,335; *The Reproduction of Color*, by R. W. G. Hunt, John Wiley and Sons, Inc., 1967; and the like. Not all compounds defined as p-phenylenediamines, however, were found to produce dye image of good quality. For example, it is stated in *The Theory of the Photographic Process* by C. E. K. Mees, 1954, at 593 that the only p-phenylenediamines that fulfill the basic requirements for color-forming developing agents are those that are unsymmetrically disubstituted such as those having the formula:



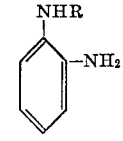
(1)

Those p-phenylenediamines with fewer than two substituents possess the necessary reduction potential and undergo the coupling reaction but have failed to yield dye images of satisfactory quality. Compounds of this type are represented by the formula:



(2)

I have now found that highly desirable photographic image dyes can be produced by reacting photographic color couplers, with oxidized p-sulfonamidoanilines (of formula 2) in the presence of or by subsequent reaction with a positively charged compound, such as an 'onium compound and preferably a quaternary compound to form an 'onium indo-N-arylsulfoaniline. I have also found that useful dyes can be formed when the sulfonamido group is ortho (of formula 3) to the amino group:



(3)

The dyes can be formed very easily and rapidly to give dye images having good stability and improved spectrophotometric properties. The dyes formed by this method are stable to light and heat and in many embodiments they are substantially unaffected by the pH changes associated with most photographic elements. Moreover, the dyes have desirable spectrophotometric properties including useful absorption maxima within the visible spectrum, narrow band widths and high extinction coefficients.

In addition, the 'onium indo-N-arylsulfoanilines appear to overcome some of the problems occurring with prior-art image dyes in photographic elements, especially where the element is washed or remains wet for extended periods; the 'onium indo-N-arylsulfoanilines formed with a polymeric 'onium compound do not appear to wash out or migrate as readily as other dyes.

In one embodiment, this invention relates to new compositions of matter which can be characterized as 'onium indo-N-arylsulfoanilines.

In another embodiment, this invention relates to photographic processes of forming 'onium indo-N-arylsulfoanilines by reacting photographic color couplers with an oxidized o- or p-sulfoanilines.

In another embodiment, this invention relates to photographic processes of forming 'onium indo-N-arylsulfoanilines by reacting photographic color couplers with an oxidized o- or p-sulfonamidoaniline in the presence of an 'onium compound.

In a preferred embodiment, this invention relates to a photographic element comprising a support and a layer thereon containing a blue-sensitive silver halide composition having associated therewith a yellow color coupler, a layer containing a green-sensitive silver halide emulsion having associated therewith a magenta color coupler and a layer containing a red-sensitive silver halide emulsion having associated therewith a cyan color coupler, wherein said element is processed in a silver halide developing composition wherein the color developing agent is predominantly a o- or p-sulfonamidoaniline or wherein said photographic element comprises an incorporated o- or p-sulfonamidoaniline developing agent in at least one layer. In certain preferred variations thereof, the element also contains an 'onium salt and more preferably a quaternary ammonium salt in at least one layer thereof.

In another preferred embodiment, the dyes of this invention can be formed in image transfer elements containing color couplers by development in a color developer containing a o- or p-sulfonamidoaniline in the presence of or with subsequent treatment with a positively charged compound such as a quaternary ammonium salt to form improved transfer images.

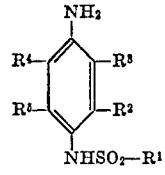
FIGS. 1–3 which form a part of the specification are spectral absorption curves of several dyes according to this invention. FIG. 4 represents spectral absorption curves of dyes produced in an image transfer system. Further details with respect to the specific dyes represented in FIGS. 1–4 are set forth in the examples.

The dyes of this invention can be generally referred to as 'onium indo-N-arylsulfoanilines and can generally be represented by the formula:

$$[(COUP)=N—Ar—N—SO_2R^1]^{\ominus}M^{\oplus}$$

wherein M is an 'onium group including sulfonium and phosphonium groups and preferably is a quaternary ammonium group; Ar is an arylene group containing 6 to 20 carbon atoms including substituted and unsubstituted arylene groups, fused-ring substituents and the like, and is preferably a phenylene group which can be substituted with alkyl or alkoxy groups wherein the alkyl group and the alkyl portion of the alkoxy group have from 1–8 carbon atoms and halogen atoms e.g. chlorine, bromide etc. or groups containing halogen atoms; and R^1 is a substituted or unsubstituted alkyl of 1–8 carbon atoms, an aryl group of 6–20 carbon atoms or heterocyclic group of 5 or 6 carbon atoms. COUP is a color-forming coupler radical linked through a carbon atom such as a radical from a phenolic coupler, a pyrazolone coupler, couplers having open-chain active methylene groups and the like, including ballasted couplers which are generally insoluble in aqueous media, diffusible couplers which can have solubilizing groups attached thereto, and the like.

The o- or p-sulfonamidoanilines which can be reacted in the oxidized form to provide the indo-N-arylsulfoaniline dye intermediates of this invention are generally any substituted or unsubstituted o- or p-sulfonamidoanilines in either the free amine or acid salt form. Free amines of suitable p-sulfonamidoanilines are represented by the formula:



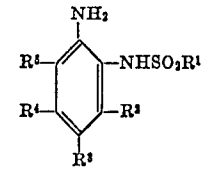
wherein R^1 is an alkyl group of 1–8 carbon atoms such as methyl, ethyl, propyl, etc., or an aryl group or substituted aryl group wherein the aryl group has from 6–20 carbon atoms such as phenyl, napthyl, toluene, etc., or R^1 may be a 5 or 6 membered heterocyclic group. R^2 and R^3, may be hydrogen, alkyl, alkoxy or halogen wherein the alkyl group and the alkyl portion of the alkoxy group have from 1–8 carbon atoms and preferably 1–4 carbon atoms and R^4 or R^5 may be any of R^2 or R^3 as well as when R^4 and R^5 are taken together, a 5 or 6 membered carbocyclic ring that may be substituted with any of R^2 or R^3.

Exemplary p-sulfonamidoanilines according to this formula are:

2-methoxy-4-benzenesulfonamidoaniline,
3-methoxy-4-benzenesulfonamidoaniline,
5-methoxy-4-benzenesulfonamidoaniline,
6-methoxy-4-benzenesulfonamidoaniline,
2,5-dimethoxy-4-benzenesulfonamidoaniline,
2,6-dimethoxy-4-benzenesulfonamidoaniline,
2-ethoxy-4-benzenesulfonamidoaniline,
3-butoxy-4-benzenesulfonamidoaniline,
5-octoxy-4-benzenesulfonamidoaniline,
2,5-diethoxy-4-benzenesulfonamidoaniline,
2,6-diethoxy-4-benzenesulfonamidoaniline,
5-bromo-2-methoxy-4-benzenesulfonamidoaniline,
6-bromo-2-ethoxy-4-benzenesulfonamidoaniline,
5-bromo-3-methoxy-4-benzenesulfonamidoaniline salt,
6-bromo-3-oxtoxy-4-benzenesulfonamidoaniline salt,
5-chloro-2-pentoxy-4-benzenesulfonamidoaniline,
6-chloro-2-methoxy-4-benzenesulfonamidoaniline,
5-chloro-3-methoxy-4-benzenesulfonamidoaniline,
6-chloro-3-methoxy-4-benzenesulfonamidoaniline,
2-methyl-4-benzenesulfonamidoaniline,
3-methyl-4-benzenesulfonamidoaniline,

5-butyl-4-benzenesulfonamidoaniline,
6-octyl-4-benzenesulfonamidoaniline,
2-ethyl-4-benzenesulfonamidoaniline,
5-ethyl-4-benzenesulfonamidoaniline,
2,5-dimethyl-4-benzenesulfonamidoaniline,
2,6-dimethyl-4-benzenesulfonamidoaniline,
3,5-dimethyl-4-benzenesulfonamidoaniline,
3,6-dimethyl-4-benzenesulfonamidoaniline,
2,5-diethyl-4-benzenesulfonamidoaniline,
2,6-dibutyl-4-benzenesulfonamidoaniline,
3,5-dihexyl-4-benzenesulfonamidoaniline,
3,6-dioctyl-4-benzenesulfonamidoaniline,
2-methoxy-4-(2-thiophenesulfonamido)aniline,
2,5-dimethoxy-4-(2-thiophenesulfonamido)aniline,
5-bromo-2-methoxy-4-(2-thiophenesulfonamido)aniline,
2-methyl-4-(2-thiazolesulfonamido)aniline,
2,6-diethoxy-4-(2-thiazolesulfonamido)aniline,
2-methoxy-4-(1-benzene-5-tetrazolesulfonamido)aniline,
2-ethyl-4-(1-benzene-5-tetrazolesulfonamido)aniline,
4-benzenesulfonamido-1-naphthylamine,
4-benzenesulfonamido-2,6-diethoxy-1-naphthylamine,
4-benzenesulfonamido-2-methyl-1-naphthylamine,
2-ethoxy-4-methanesulfonamido-1-naphthamine.

The free amines of suitable o-sulfonamidoanilines are represented by the formula:



wherein R^1, R^2, R^3, R^4 and R^5 are as defined in relation to the p-sulfonamidoanilines.

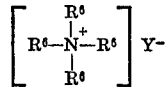
Exemplary o-sulfonamidoanilines according to this invention are:

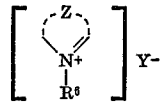
2-benzenesulfonamido-4-methoxyaniline,
2-benzenesulfonamido-4-bromoaniline,
4,6-dimethoxy-2-methanesulfonamidoaniline,
4-methoxy-2-(4-methylbenzenesulfonamido)aniline.

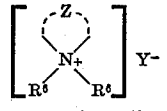
'Onium compounds have been used in the photographic art for quite some time. For example, U.S. Pat. 2,648,604 discloses the use of non-surface-active quaternary compounds as development accelerators, and U.S. Pats. 2,271,623, 2,271,622 and 2,275,727 disclose the use of quaternary ammonium, quaternary phosphonium and tertiary sulfonium compounds as sensitizers for silver halide emulsions. Moreover, U.S. Pats. 3,146,102 and 3,212,893 disclose the use of 'onium compounds in combination with dye developers in image transfer systems. Nevertheless, there does not appear to be any recognition in the art of the highly useful 'onium indo-N-arylsulfonaniline dyes as set forth in this invention.

In one embodiment, especially useful dye images have been obtained through the combination of the indo-N-arylsulfoaniline intermediate and quaternary ammonium compounds to form the 'onium indo-N-arylsulfoaniline dye images. As is known, quaternary ammonium compounds are organic compounds containing a pentavalent nitrogen atom. Generally, they can be considered as derivatives of ammonium compounds wherein the four valences usually occupied by the hydrogen atoms are occupied by organic radicals. Generally, the organic radicals are joined directly to the pentavalent nitrogen through a single or double carbon-to-nitrogen bond. The term "quaternary ammonium," as used herein, is intended to cover compounds wherein the pentavalent nitrogen is one of the nuclear atoms in a heterocyclic ring, as well as those wherein each of the four vacancies is attached to separate organic radicals, e.g., tetraalkyl quaternary am-

monium compounds. Useful quaternary ammonium compounds can be represented by the following formulae:

(1) 

(2) 

(3) 

wherein each R^6 is an organic radical, Y is an anion, e.g., hydroxy, bromide, chloride, toluenesulfonate, etc., and Z represents the atoms necessary to complete a heterocyclic ring. Examples of compounds within Formulae 1, 2 and 3 include tetraethylammonium bromide, N-ethylpyridinium bromide, N,N-diethylpiperidinium bromide, ethylene-bis-pyridinium bromide, 1-ethyl-pyridinium bromide, 1-phenethyl - 3 - picolinium bromide, tetraalkylammonium salts, cetyltrimethylammonium bromide, polyalkylene oxide bis-quaternary ammonium salts such as polyethylene oxide bis-pyridinium perchlorate, the heterocyclic quaternary ammonium salts mentioned which form the methylene bases including 3-methyl-2-ethylisoquinolinium bromide, 3-methylisoquinolinium methyl-*p*-toluenesulfonate, 1-ethyl-2-methyl - 3 - phenethylbenzimidazolium bromide, 5,6-dichloro - 1 - ethyl - 2 - methyl-3-(3-sulfobutyl)-benzimidazolium betaine and the pyridinium salts below.

Other useful 'onium compounds include tertiary sulfonium and quaternary phosphonium compounds represented by the formulae:

(4) $(R^6)_3S^+X^-$

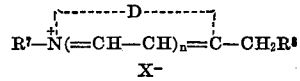
and

(5) $(R^6)_4P^+X^-$

wherein each R^6 is an organic radical, e.g., alkyl, aralkyl, aryl, etc., groups, and X is an anion, e.g., hydroxy, bromide chloride, toluenesulfonate, etc. Typical tertiary sulfonium and quaternary phosphonium compounds include lauryldimethylsulfonium *p*-toluenesulfonate, nonyldimethylsulfonium *p*-toluenesulfonate and octyldimethylsulfonium *p*-toluenesulfonate, butyldimethylsulfonium bromide, triethylsulfonium bromide, tetraethylphophonium bromide, dimethylsulfonium *p*-toluenesulfonate, dodecyldimethylsulfonium *p*-toluenesulfonate, decyldimethylsulfonium *p*-toluenesulfonate and ethylene-bis-oxymethyltriethylphosphonium bromide.

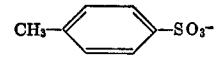
The 'onium compounds may be used as the hydroxide or as the salt. When the 'onium compounds are used as the salt, the anion may be a derivative of any acid. However, it should be noted that when the anion is iodide, such iodide may have deleterious effects on the emulsion and suitable precautions should be taken if it is to be in contact with the emulsion before development is complete. Especially good results are obtained when the 'onium compounds employed are bromides.

Useful heterocyclic quaternary ammonium compounds which are methylene bases diffusible in alkaline solution have the general formula:

(6) 

wherein D represents the nonmetallic atoms necessary to complete the heterocyclic nucleus of the quaternary ammonium compound containing 1 or more of the reactive methyl groups $—CH_2R'$ in one or more of the nuclear positions, the other nuclear positions being substituted or not, such as quaternary salts of the pyridine, quinoline,

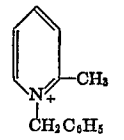
benzoquinoline, benzoxazole, benzoselenazole, thiazole, benzothiazole, naphthothiazole, benzimidazole, isoquinoline series, etc.; *n* is 0 or 1; R^7 is an alkyl group, an aryl or aralkyl group of the benzene series, or substituted alkyl, aryl or aralkyl groups of the benzene series, the alkyl chains preferably being lower alkyl of from 1 to 4 carbon atoms; R^8 is a hydrogen atom or one of the groups represented by R^7 and X represents OH— or an acid anion such as Br—, CH_3SO_4— or



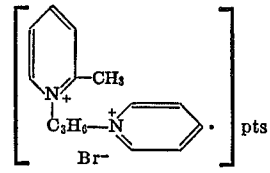
One or more of these quaternary ammonium compounds can be used alone or in combination with the 'onium compounds having the Formulae 1, 2, 3, 4 and 5 above, and are advantageously employed in either the processing solution, the photographic element, or both.

Typical 'onium salts which are useful in the invention which form diffusible methylene bases are as follows:

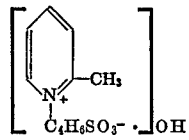
1-benzyl-2-picolinium bromide



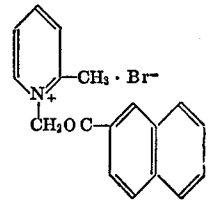
1-(3-bromopropyl)-2-picolinium *p*-toluenesulfonate
1-phenethyl-2-picolinium bromide
1-γ-phenylpropyl-2-picolinium bromide
2,4-dimethyl-1-phenethylpyridinium bromide
2,6-dimethyl-1-phenethylpyridinium bromide
5-ethyl-2-methyl-1-phenethylpyridinium bromide
2-ethyl-1-phenethylpyridinium bromide
1-[3-(N-pyridinium bromide)propyl]-2-picolinium *p*-toluenesulfonate



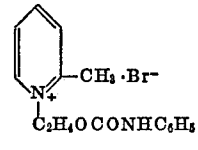
anhydro-1-(4-sulfobutyl)-2-picolinium hydroxide



α-picoline-β-naphthoylmethyl bromide



1-β-phenylcarbamoyloxyethyl-2-picolinium bromide



1-methyl-2-picolinium *p*-toluenesulfonate
1-phenethyl-2,4,6-trimethylpyridinium bromide
1-phenethyl-4-n-propylpyridinium bromide
4-γ-hydroxypropyl-1-phenethylpyridinium bromide and
1-n-heptyl-2-picolinium bromide

A number of pyridinium salts having the above general formula generally useful as nondiffusible 'onium salts are:

1-n-decyl-2-picolinium bromide
1,2-dibenzylpyridinium bromide
6-amino-1-phenethyl-2-picolinium bromide
2-amino-1-phenethyl-4-picolinium bromide
2-benzyl-1-phenethylpyridinium bromide and
4-benzyl-1-phenethylpyridinium bromide

The following, which do not form methylene bases in alkali solutions, also can be used:

1-phenethylpyridinium bromide
1-ethylpyridinium bromide
1-phenethyl-3-picolinium bromide and
1-n-nonylpyridinium *p*-toluenesulfonate

In one embodiment of the invention, the image dye is mordanted in a polymeric material such as a polymer with 'onium groups thereon. Typical useful mordants of this type are vinylpyridinium compounds of the type disclosed in U.S. Pat. 2,484,430; polymers containing quaternary ammonium groups such as disclosed in U.S. Pats. 3,625,694, 3,758,445, 3,709,690, 3,693,357, 3,488,706, and 3,557,006; and the like.

In another embodiment, the mordant is an 'onium coacervate mordant such as disclosed in Bush, U.S. Pat. 3,271,147 issued Sept. 6, 1966.

The 'onium salts can be used in concentrations necessary to form an 'onium indo-N-arylsulfoaniline with all of the indo-N-arylsulfoaniline present in a photographic element. When the 'onium compound is immobile or ballasted and present in an image layer, it is generally utilized in concentrations of about 25 mg. to about 1000 mg. per square foot, and preferably about 50 to about 500 mg. per square foot, depending of course, on the ratio of 'onium atoms to molecular weight of the compound employed. When the 'onium salt is supplied by a solution such as in the processing solution, typical useful concentrations range from .01% by weight to about 5% by weight of the 'onium compound to provide complete reaction, again depending on the concentration of the dye in the photographic element and the ratio of 'onium groups to molecular weight of the 'onium compound.

The 'onium indo-N-arylsulfoanilines can generally be formed in situ in any of the color systems employing color-forming couplers; several exemplary systems are disclosed by Weissberger, "A Chemist's View of Color Photography" *American Scientist,* vol. 58, No. 6, November-December 1970, pp. 648–660.

In the photographic systems of this invention, the couplers, developers and 'onium salts can be incorporated in various layers of the element in water-permeable association, or the respective ingredients can be introduced into the element at various stages of processing. The color-forming couplers can be incorporated in the photographic element in association with a silver halide emulsion. The o- or p-sulfonamidoaniline developing agent can be contacted with the exposed silver halide emulsion after exposure by use of liquid processing composition containing the developing agent or the o- or p-sulfonamidoaniline can be incorporated in the silver halide emulsion layer wherein it can be activated by a liquid such as an alkaline solution. It is also understood that auxiliary developing agents such as pyrazolidones, ascorbic acids, p-phenylene diamines and the like can be used in the process, if desired, to achieve variations in image properties and development characteristics.

The couplers which are generally useful in producing the 'onium indo-N-arylsulfoanilines of this invention include those compounds which have an active coupling group which will react with an oxidized aromatic primary amine, such as exemplified by the many couplers which have been used in the prior art in combination with p-phenylenediamines. The couplers of this invention include the diffusible as well as nondiffusible type.

The term "nondiffusing" used herein as applied to the couplers has the meaning commonly applied to the term in color photography and denotes materials which for all practical purposes do not migrate or wander through organic colloid layers, such as gelatin, comprising the sensitive elements of the invention.

The term "diffusible" as applied to the dyes formed from the "nondiffusing" couplers in this invention has the converse meaning and denotes materials having the property of diffusing effectively through the colloid layers of the sensitive elements in the presence of the "nondiffusing" materials from which they are derived. Typical useful couplers include compounds having open-chain active methylene groups, pyrazolone compounds, phenolic compounds and the like which, when reacted with an oxidized o- or p-sulfonamidoaniline, form an indoaniline compound, i.e., indoaniline, azomethines and the like.

The compounds referred to herein as couplers contain a "coupling position" which is generally known to those skilled in the art as being the position on the coupler molecule that reacts or couples with oxidized color developing agents. Typical useful couplers, include phenolic couplers, including -naphthols which couple at the 4-position, open-chain ketomethylene couplers which couple at the carbon atom forming the methylene moiety, e.g.,

wherein * denotes the coupling position, 5-pyrazoline couplers which couple at the carbon atom in the 4-position, and the like. Typical specific diffusible coupler compounds which can be reacted with oxidized o- or p-sulfonamidoanilines to form the image dye intermediate according to this invention are disclosed in U.S. Pats. 2,407,210 by Weissberger et al. issued Sept. 3, 1946; 2,298,443 by Weissberger issued Oct. 13, 1942; 2,875,057 by McCrossen et al. issued Feb. 24, 1959; 3,265,506 by Weissberger et al. issued Aug. 9, 1966; 3,408,194 by Loria issued Oct. 29, 1968; 3,447,928 by Loria issued June 3, 1969; 2,369,489 by Porter et al. issued Feb. 13, 1945; 2,600,788 by Loria et al. issued June 17, 1952; 2,908,573 by Bush et al. issued Oct. 13, 1959; 3,062,653 by Weissberger et al. issued Nov. 6, 1962; 3,419,391 by Young issued Dec. 31, 1968; 3,519,429 by Lestina issued July 7, 1970; 3,152,896 by Tuite issued Oct. 13, 1964; 2,423,730 by Salminen et al. issued July 8, 1947; 2,474,293 by Weissberger et al. issued June 28, 1949; 3,476,563 by Loria issued Nov. 4, 1969; 2,772,162 by Salminen et al. issued Nov. 27, 1956; and 3,002,836 by Vittum et al. issued Oct. 3, 1961; which are all incorporated herein by reference.

Nondiffusible couplers including the Fischer-type couplers and the like, can be used for example, as exemplified by the cyan-forming dye couplers disclosed in Loria, U.S. Pat. 2,476,563 issued Nov. 4, 1969.

Typical useful nondiffusible compounds especially useful in the image transfer systems of this invention include the nondiffusible couplers having the formulas:

$$\text{BALL—LINK—(COUP—SOL)}_n$$

and

$$\text{SAID—LINK—(COUP—BALL)}_n$$

wherein:

(1) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render such coupler nondiffusible during development in an alkaline processing composition;

(2) LINK is a connecting radical which will split when contacted with an oxidized silver halide developer, and is preferably an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical, an azoxy radical, an aminoalkyl radical as disclosed in Cressman et al., U.S. Pat. 3,419,390, a sulfonyloxy radical as disclosed in Porter, U.S. Pat. 3,415,652, an acyloxy radical as disclosed in Loria, U.S. Pat.

3,311,476, and an imido radical as disclosed in Loria, U.S. Pat. 3,458,315;

(3) COUP is a coupler radical such as a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, COUP substituted in the coupling position with LINK;

(4) SOL is a hydrogen atom or an acidic solubilizing group when the color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when the color developing agent is free of an acidic solubilizing group, and;

(5) SAID is an o- or p-sulfonamidoaniline image dye precursor, and;

(6) *n* is generally an integer of 1, provided that when LINK is an alkylidene radical *n* can be an integer of 1 or 2.

Acidic solubilizing radicals are generally attached to the diffusible moiety of the compounds described, which can be solubilizing radicals which, when attached to the dye-providing moiety, render the dyes diffusible in alkaline processing compositions. Typical of such radicals are carboxylic, sulfonic, ionizable sulfonamide and hydroxy-substituted groups that lend to dyes negative charges.

The nature of the ballast groups in the diffusible dye-producing compounds described above (BALL—) is not critical as long as they confer nondiffusibility to the coupler compounds. Typical ballast groups include long-chain alkyl radicals linked directly or indirectly to the coupler molecules, as well as aromatic radicals of the benzene and naphthalene series, etc., linked directly or indirectly to the coupler molecules by a splittable linkage, or by a removable or irremovable but otherwise nonfunctional linkage depending upon the nature of the coupler compound. Generally, useful ballast groups have at least 8 carbon atoms.

In one embodiment of this invention, the new dyes can be formed in negative, direct positive or reversal color processes. The coupler can be incorporated in the photographic element and preferably contains a ballast group to immobilize the coupler and prevent migration when it is located in a multi-color element. A o- or p-sulfonamidoaniline developer is used at the appropriate stage, depending on the type of system, to develop the exposed silver halide whereby the oxidized o- or p-sulfonamidoaniline can react with the color-forming coupler. In the embodiments where a minimum number of solubilizing groups are placed on the coupler and the sulfonamidoaniline contains no substantial additional solubilizing groups, the coupler need not be ballasted as the coupled reaction product will generally be insoluble. The reaction product dye intermediate is formed in the presence of, or subsequently treated with, a positively charged compound such as an 'onium salt to form the desired image dye. It will be appreciated, of course, that the solubility of the coupler and the o- or p-sulfonamidoaniline developer will depend on the desired characteristics of the photographic system, the degree of tolerable color contamination, the type of barrier layer employed in the system, and the like.

In another embodiment, water-soluble color couplers are added to the emulsion prior to or during the color developing step wherein the respective color coupler will react with the oxidized sulfonamidoaniline to form the onium N-arylsulfoaniline. The onium N-arylsulfoaniline is then contacted with the 'onium compound to form the 'onium indo-N-arylsulfoaniline which yields the desired image dye. In embodiments of this type, silver halide layers sensitized to different colors can be developed sequentially to obtain the desired color in each layer or they can be developed simultaneously, for example when emulsions sensitized to different colors are coated on opposite sides of a film support.

In another embodiment, the dyes of this invention can be formed in image transfer processes. In one image transfer system a silver halide emulsion having associated therewith a non-diffusible color coupler is reacted with a o- or p-sulfonamidoaniline to form a diffusible indo-N-arylsulfoaniline which is reacted with an onium compound to form an 'onium indo-N-arylsulfoaniline image dye. In another image transfer system, a silver halide emulsion has associated therewith a diffusible color coupler. After imagewise exposure the coupler is immobilized imagewise during development with portions of the diffusible coupler diffusing to an image receiving layer where it is reacted with the oxidized o- or p-sulfonamidoaniline developing agent in association with an onium compound to provide the 'onium N-arylsulfonamidoaniline image dye. Typical image transfer formats where the present invention can be utilized are disclosed in U.S. Pats. 3,227,550, 3,227,552, 3,415,644, 3,415,645 and 3,415,646 and Belgian Pats. 757,959 and 757,960; both issued Apr. 23, 1971.

In addition the o- or p-sulfonamidoaniline intermediates prepared in accordance with the present invention can be utilized to form various photographic image dye providing compounds such as those containing oxichromic dye precursors, preformed dyes, shifted dyes, etc., which can be utilized in photographic image transfer systems. For example, the o- or p-sulfonamidoaniline groups can provide the dye or dye precursor moiety of the initially diffusible dye image providing materials of Bush and Reardon, U.S. Ser. No. 227,113 filed Feb. 17, 1972 and Bush and Lestina, U.S. Ser. No. 206,836 now abandoned or the dye moiety or dye precursor moiety of the initially nondiffusible image dye providing compounds of Fleckenstein and Figueras, U.S. Ser. No. 176,751 now abandoned, Anderson and Lum, U.S. Pat. No. 3,725,062 issued Apr. 3, 1973, U.S. Pat. No. 3,698,879 issued Oct. 17, 1972, Pat. No. 3,728,113 issued Apr. 17, 1973, Whitmore et al., U.S. Pat. 3,227,552 issued Jan. 4, 1966, Porter U.S. Pat. 3,415,-652, Loria U.S. Pats. 3,311,476 and 3,432,521 and Whitmore U.S. Pat. 3,227,550 as well as those disclosed in Bloom et al., U.S. Pats. 3,443,939, 3,443,940 and 3,443,941.

The silver halide emulsions used with this invention can comprise silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. The emulsions may be course- or fine-grain and can be prepared by any of the well-known procedures, e.g., single-jet emulsions, double-jet emulsions, such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in U.S. Pats. 2,222,264 by Nietz et al., 3,320,069 by Illingsworth, and 3,271,157 by McBride. Surface-image emulsions can be used or internal-image emulsions can be used such as those described in U.S. Pats. 2,592,250 by Davey et al., 3,206,313 by Porter et al., and 3,447,927 by Bacon et al. The emulsions may be regular-grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci.*, vol. 12, No. 5, September/October 1964, pp. 242–251. If desired, mixtures of surface- and internal-image emulsions can be used as described in Luckey et al., U.S. Pat. 2,996,382.

Negative-type emulsions can be used or direct-positive emulsions can be used such as those described in U.S. Pats. 2,184,013 by Leermakers, 2,541,472 by Kendall et al., 3,367,778 by Berriman, 2,563,785 by Ives, 2,456,953 by Knott et al. and 2,861,885 by Land, British Pat. 723,019 by Schouwenaars, and U.S. Pat. 3,501,307 by Illingsworth.

The silver halide emulsions may be unwashed or washed to remove soluble salts. In the latter case, the soluble salts may be removed by chill-setting and leaching or the emulsion may be coagulation-washed, e.g., by the procedures described in U.S. Pats. 2,618,556 by Hewitson et al., 2,614,928 by Yutzy et al., 2,565,418 by Yackel, 3,241,969 by Hart et al., and 2,489,341 by Waller et al.

Also, the silver halide emulsions may contain speed-increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in U.S. Pats. 2,886,437 by Piper, 3,046,134 by Dann et al., 2,944,900 by Carroll et al., and 3,294,540 by Goffe.

Likewise, the silver halide emulsions can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in U.S. Pats. 2,131,038 by Brooker et al. and 2,694,716 by Allen et al.; the azaindenes described in U.S. Pats. 2,886,437 by Piper and 2,444,605 by Heimbach et al.; the mercury salts as described in Allen et al., U.S. Pat. 2,728,663; the urazoles described in Anderson et al., U.S. Pat. 3,287,135; the sulfocatechols described in Kennard et al., U.S. Pat. 3,236,652; the oximes described in Carroll et al., British Pat. 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in U.S. Pats. 2,403,927 by Kendall et al., 3,266,897 by Kennard et al., and 3,397,987 by Luckey et al.; the polyvalent metal salts described in Jones, U.S. Pat. 2,839,405; the thiuronium salts described in Herz et al., U.S. Pat. 3,220,839; the palladium, platinum and gold salts described in U.S. Pats. 2,566,263 by Trivelli et al. and 2,597,915 by Yutzy et al. and the tetrazoles described in Hoppe U.S. Pat. 3,352,672.

The invention can be further illustrated by the following examples.

EXAMPLE 1

(A) A supported, single-layer, gelatino silver halide emulsion coating, containing per square foot of coating 100 mg. silver, 300 mg. gelatin, 135 mg. of the yellow-dye-forming coupler α-[3-{α - (2,4-di-*tert*-amylphenoxy) butyramido}-benzoyl]-2-methoxyacetanilide and 68 mg. of the coupler solvent di-n-butyl phthalate, is exposed to a graduated-density test object and developed for 20 minutes at a temperature of 22° C. in a color developing solution of the following composition:

2 - methoxy - 4 - phenylsulfonamidoaniline hydrochloride	g--	2.6
Sodium carbonate	g--	20.0
Potassium bromide	g--	1.0
Sodium sulfite	g--	2.0
Ethyl alcohol	ml--	15.0

Water to 1 liter.
pH of 12.5.

The sample is conventionally fixed, washed, bleached, washed, fixed, washed and dried.

The spectrophotometric profile of the resulting indoaniline dye is illustrated by Curve Y in FIG. 1. The curve shows that the dye is unsuited as a yellow image dye.

(B) The coating containing the dye image resulting from step (A) above is then immersed for 1 minute in 1 liter of an aqueous solution (pH, 10.0) containing 0.5 g. of the 'onium compound laurylpyridinium *p*-toluenesulfonate, washed and dried. The so-treated sample now contains an 'onium indo-N-arylsulfoaniline dye image whose spectrophotometric profile is represented by Curve Y' in FIG. 1. The curve represents a dye which has excellent spectrophotometric properties as a yellow image dye.

The above spectrophotometric readings are made at the highest dye density ($D_{max.}$) areas in each of the two samples. The maximum density point ($D_{max.}$) of the dye represented by Curve Y in FIG. 1 lies outside the visible region of the electromagnetic spectrum, i.e., in the U.V. region of the spectrum. The point therefore cannot be recorded on the conventional graph paper. The maximum density point of the dye represented by Curve Y' ($D_{max.}$=0.3) lies at the desirable wavelength ($\lambda_{max.}$) for a yellow dye of about 450 nm. (nanometers). Moreover, the dye represented by Curve Y' has relatively little unwanted absorption in the green and red regions of the spectrum.

(C) Similar results are obtained when laurylpyridinium p-toluenesulfonate is present in the color developing solution and the post-treatment of the coating in a separate bath is omitted.

EXAMPLE 2

The procedure described in Example 1 is repeated with a similar coating containing the cyan-dye-forming coupler 1-(2,4,6-trichlorophenyl)-3-[2-chloro-5-(α-(4-hydroxy-3-*tert* - butylphenoxy)tetradecanoamido)anilino]-5-pyrazolone. The results are illustrated in FIG. 2 (see Curves M, M').

Curve M represents an indoaniline dye which is unsuited as a magenta image dye because of its low absorption in the green and relatively high absorption in the blue regions of the spectrum. Curve M' represents an 'onium indo-N-arylsulfoaniline dye which has desirable spectrophotometric properties as a magenta image dye. The spectrophotometric readings again are made at the $D_{max.}$ areas in each of the two samples.

EXAMPLE 3

The procedure described in Example 1 is repeated with a simple coating containing the cyan-dye-forming coupler 1 - hydroxy-2-[Δ-(2,4-di-*tert*-amylphenoxy)-n-butyl]naphthamide. The results are illustrated in FIG. 3 (see Curves C and C').

Curve C represents an indoaniline dye which is unsuited as a cyan image dye because of its low absorption in the red and very high absorption in the green and blue regions of the spectrum. Curve C' represents an 'onium indo-N-arylsulfoaniline dye which has desirable spectrophotometric properties as a cyan image dye. The dye has a very high extinction coefficient, narrow band width and low absorption in the blue and red regions of the spectrum.

EXAMPLE 4

A multilayer photographic element is prepared comprising a film support coated in succession with a red-sensitive gelatino silver chlorobromide emulsion layer (100 mg. Ag and 300 mg. gel/ft.^{2}) containing the cyan dye-forming coupler 1-hydroxy-2-[Δ-(2,4-di-*tert*-amylphenoxy)-n-butyl]naphthamide (110 mg./ft.^{2}) and the coupler solvent tricresyl phosphate (55 mg./ft.^{2}); a gel interlayer; a green-sensitive gelatino silver chlorobromide emulsion layer (100 mg. Ag and 300 mg. gel/ft.^{2}) containing the magenta dye-forming coupler 1-(2,4,6-trichlorophenyl)-3-[2 - chloro-5-(α-(4-hydroxy-3-*tert*-butylphenoxy) tetradecanoamido) anilino]-5-pyrazolone (168 mg./ft.^{2}) and the coupler solvent tricresyl phosphate (84 mg./ft.^{2}); a gel interlayer containing 15 mg./ft.^{2} Carey Lea silver; a blue-sensitive gelatino silver chlorobromide emulsion layer (100 mg. Ag and 300 mg. gel/ft.^{2}) containing the yellow dye-forming coupler α-[3-(α-(2,4-di-*tert*-amylphenoxy)butyramido)-benzoyl] - 2 - methoxyacetanilide (135 mg./ft.^{2}) and the coupler solvent di-n-butyl phthalate (68 mg./ft.^{2}); and a gelatin overcoat layer (50 mg./ft.^{2}).

The element is then exposed to a multicolor test object. A reddish-brown dye image results when subjected to the process described in Example 1(A); however, when this sample is further treated according to the procedure described in Example 1(B), a useful negative color dye image is obtained.

EXAMPLES 5 THROUGH 9

Several multilayer elements as described in Example 4 are prepared and are subjected to the process of Example 1 (A) and (B) except that the 2-methoxy-4-benzenesul-

fonamidoaniline hydrochloride is replaced with the following p-sulfonamidoanilines color developing agents:

Example	p-Sulfonamidoaniline
(5)	3 - methoxy - 4 - benzenesulfonamidoaniline hydrochloride,
(6)	2,5-dimethoxy - 4 - benzenesulfonamidoaniline hydrochloride,
(7)	5-bromo-3-methoxy - 4 - benzenesulfonamidoaniline hydrochloride,
(8)	6-chloro-3-methoxy - 4 - benzenesulfonamidoaniline hydrochloride,
(9)	3,6-dimethyl - 4 - benzenesulfonamidoaniline hydrochloride.

In each example the resulting multicolor dye image has excellent spectrophotometric properties for use as a photographic negative color dye image.

EXAMPLE 10

Separate samples of a receiving sheet comprising a cellulose acetate film support on which is coated a dye mordanting layer containing copoly[styrene-N-benzyl-N,N - dimethyl-N-(3-maleimidopropyl)ammonium chloride] (200 mg./ft.^{2}) and gelatin (200 mg./ft.^{2}) are swabbed with a viscous developing composition containing:

4-benzenesulfonamido - 2 - methoxyaniline hydrochloride	g	0.314
Hydroxyethylcellulose	g	1.2
0.25 M_3K_4PO	ml	50

Separate samples of the above receiving element are then brought into contact with the following imagewise exposed single layer silver halide coatings on a cellulose acetate support.

(D) Blue-sensitive negative silver halide emulsion layer (150 mg. Ag and 400 mg. gel/ft.^{2}) containing the yellow image transfer coupler, α-pivalyl-α[4-(N-methyl-N-n-octadecylsulfamyl)phenoxy] - 2 - chloro-4-sulfamylacetanilide (136 mg./ft.^{2}).

(E) Green-sensitive negative silver halide emulsion (150 mg. Ag and 400 mg. gel/ft.^{2}) containing the magenta image transfer coupler, 1-phenyl-3-(3,5-dicarboxyanilino)-4-(m-octadecylcarbonylphenylthio) - 5 - pyrazolone (132 mg./ft.^{2}).

(F) Red-sensitive negative silver halide emulsion (150 mg. Ag and 400 mg. gel/ft.^{2}) containing the cyan image transfer coupler, 1-hydroxy-4-{4'-[α-(3''-pentadecylphenoxy)butyramido]-phenoxy} - N-ethyl - N-2''',5'''-dicarboxynaphthanilide (152 mg./ft.^{2}).

After several minutes, the elements are separated and well-defined yellow, magenta and cyan dye images, are produced on the receivers. Spectral absorption curves of these dye images produced by the coatings D, E and F are illustrated in FIG. 4.

This invention has been described in detail with particular reference to certain preferred embodiments thereof, but there will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A process of forming an 'onium indo-N-arylsulfoaniline in a color coupler-containing silver halide emulsion layer which comprises reacting said color coupler with an imagewise oxidized o- or p-sulfonamidoaniline and reacting the resulting dye with an 'onium compound.

2. A process according to claim **1** wherein said 'onium compound is a quaternary amonium salt.

3. A process of forming an 'onium indo-N-arylsulfoaniline dye image in an imagewise exposed photographic element which comprises (1) a support, and (2) at least one layer thereon containing a silver halide emulsion having in association therewith a photographic color coupler, said process comprising contacting said exposed photographic element with a developing composition comprising a o- or p-sulfonamidoaniline color developing agent in the presence of an 'onium compound.

4. A process according to claim **3** wherein said 'onium compound is present in at least one layer of said photographic element.

5. A process according to claim **3** wherein said photographic element comprises a layer comprising a blue-sensitive silver halide emulsion in association with a yellow dye forming color coupler, a layer comprising a green-sensitive silver halide emulsion in association with a magenta dye forming color coupler and a red-sensitive silver halide emulsion in association with a cyan dye forming color coupler.

6. A process according to claim **5** wherein said silver halide emulsions are fogged, direct-positive, silver halide emulsions.

7. A process according to claim **5** wherein said silver halide emulsions are unfogged, silver halide emulsions.

8. A process according to claim **5** wherein said color couplers are nondiffusing color couplers.

9. A process according to claim **5** wherein said photographic element comprises at least one layer containing said 'onium compound.

10. A process according to claim **3** wherein said 'onium compound is a quaternary ammonium salt, a tertiary sulfonium salt or a quaternary phosphonium salt.

11. A process according to claim **3** wherein said 'onium compound is provided in sufficient concentration to combine with substantially all of the reaciton product of oxidized o- or p-sulfonamidoaniline and color coupler.

12. A process of forming an 'onium transfer image comprising (a) imagewise exposing a photographic element comprising a support having thereon at least one layer comprising a silver halide emulsion having associated therewith a photographic color coupler, capable of reacting with an oxidized aromatic primary amino color developing agent to produce a diffusible dye, (b) treating said photographic element with a developer solution to effect development wherein the color developing agent is a o- or p-sulfonamidoaniline, to form an imagewise distribution of dye image-providing material as a function of said imagewise exposure of said silver halide composition and (c) providing an 'onium compound in association with said dye image-providing material to provide an 'onium indo-N-arylsulfoaniline image dye, and at least a portion of said dye image-providing material diffusing to a dye image-receiving layer.

13. A process according to claim **12** wherein said coupler is nondiffusible and has a formula selected from the group consisting of

$$\text{BALL—LINK—(COUP—SOL)}_n$$

and

$$\text{SAID—LINK—(COUP—BALL)}_n$$

wherein:

(1) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render such coupler nondiffusible during development in an alkaline processing composition;

(2) LINK is a connecting radical which will split when contacted with an oxidized silver halide developer, and is preferably an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical, an azoxy radical, an aminoalkyl radical, a sulfonyloxy radical, an acyloxy radical, and an imido radical;

(3) COUP is a coupler radical such as a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, COUP substituted in the coupling position with LINK;

(4) SOL is a hydrogen atom or an acidic solubilizing group when the color developing agent contains an acidic solubilizing group, and SOL is an acidic solu-

bilizing group when the color developing agent is free of an acidic solubilizing group;

(5) SAID is an o- or p-sulfonamidoaniline image dye precursor; and

(6) *n* is generally an integer of 1, provided that when LINK is an alkylidene radical *n* can be an integer of 1 or 2.

14. A process according to claim **12** wherein said 'onium compound is a quaternary ammonium salt, a tertiary sulfonium salt or a quaternary phosphonium salt.

15. A process according to claim **12** wherein said 'onium compound is a polymeric quaternary ammonium salt and is located in said image-receiving layer.

16. A process according to claim **12** wherein said o- or p-sulfonamidoaniline developing agent is incorporated in at least one layer of said photographic element.

17. A photographic element comprising a support and at least one layer thereon comprising an imagewise distribution of 'onium indo-N-arylsulfoaniline.

18. A photographic element according to claim **17** wherein said 'onium indo-N-arylsulfoaniline has the formula:

$$[(COUP)=N—Ar—N—SO_2R^1]^{\ominus}M^{\oplus}$$

wherein COUP is a color coupler radical, Ar is an arylene group comprising from 6 to 20 carbon atoms, M is an 'onium group and R^1 is an alkyl, aryl or heterocyclic group.

19. A photographic element comprising at least one layer containing a silver halide emulsion, having in association therewith a color-forming coupler, at least one layer in association with said color-forming coupler which contains an 'onium compound and at least one layer containing an o- or p-sulfonamidoaniline in sufficient concentration to produce an image by reaction with said silver halide emulsion.

20. A photographic element according to claim **19** wherein said 'onium compound is a quaternary ammonium salt, a tertiary sulfonium salt or a quaternary phosphonium salt.

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